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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

THERMODYNAMICS - Condensation Theory, Vapor Equilibrium in the Presence of Drops.
Note by M. Yves Rocard, presented by M. Jean Cabannes

The modern attempts of condensation theories, either because of ignorance of the liquid stage (J. E. Mayer), or by including it (Lee and Yang), all maintain that at any given temperature T less than the critical temperature T_c they can predict an angular point of the Andrews $[P = f(\rho)]$ isotherm followed by a liquefaction level. These theories therefore offer no means of predicting super saturation, which after all is normal. In fact if H is the surface tension, the pressure P_1 will exist in the center of a drop of radius R_0 , which differs from the pressure P_2 of the vapor (density ρ_2) in $P_1 - P_2 = 2H/R_0$. Furthermore, thermodynamics in its first approximation shows that in the presence of this drop the equilibrium pressure of vapor P_2 differs from the normal pressure P of saturated vapor by $P_2 - P = (2H/R_0)(\rho_2/\rho_1)$, if ρ_1 is the liquid's density. The "discontinuity" pressure P_2 is therefore a function of T and of R , which is not foreseen by the quoted modern theories.

On the contrary, a perfectly continuous theory and one completely in conformance with the kinetic theory of gases, allows all these elements to be calculated, ρ_2 and ρ_1 , as well as $(P_2 - P)$ and $(P_1 - P_2)$, and to obtain accurate expressions, more powerful than those of thermodynamics, which assumes $\rho_2 \ll \rho_1$, the vapor being a perfect gas and the liquid being compressible and nondilatable. This theory which is based on the principles given above to explain surface tension, will be developed in another article. It allows for the following results:

Take ρ_v as the normal density of saturating vapor at T . Let us assume ρ_2 to be slightly higher than ρ_v , the density ρ_1 of the liquid in the center of a drop which would be in equilibrium with the vapor ρ_2 , with a radius R_0 to be

established, is given by the strict relation

$$P(T, \rho_1) - P(T, \rho_2) = \rho_1 \int_{\rho_2}^{\rho_1} \frac{P(T, \rho) - P(T, \rho_2)}{\rho^2} d\rho.$$

Assuming $\rho_2 = \rho_v$, ρ_1 is equal to the usual "liquid" density, $P(T, \rho_1) = P(T, \rho_2)$ and the integral of the second member is (0), a purely mechanical demonstration of the known theorem

$$\oint P dv = 0.$$

The following differential equation may be established, completely fixing the density variation starting from the center of the drop

$$\frac{\alpha \sigma^2 \lambda}{5M^2} \left[\frac{d^2 \rho}{dR^2} + \frac{1}{R} \frac{d\rho}{dR} \right] = \int_{\rho_2}^{\rho} \frac{P(T, \rho) - P(T, \rho_2)}{\rho^2} d\rho + \frac{P(T, \rho) - P(T, \rho_2)}{\rho}$$

α = constant Van der Waals internal pressure, σ , molecular diameter, M molecular mass, λ numerical constant depending only on the law of molecular attraction and equal to approximately 3 for London's law. This equation which is rigorous once λ has been correctly defined, integrated with $\rho = \rho_2$ for $R \infty$ and $d\rho/dR = 0$ for $R = 0$ defines absolutely all, especially ρ_1 for $R = 0$, as the drop center.

However if one agrees to speak of a radius R_0 of the drop, defined by $P_1 - P_2 = P(\rho_1) - P(\rho_2) = 2H/R_0$, with H calculated as in the referenced work, one may establish a useful relation between ρ_2 and R_0 which defines the size of the drop in equilibrium with the vapor of $\rho_2 > \rho_v$ density.

1° Lord Kelvin's law may be found as a first approximation for $\rho_1 \gg \rho_2$ and a vapor which acts as a perfect gas

$$P_2 - P = \frac{2H}{R_0} \cdot \frac{\rho_2}{\rho_1}.$$

2° A second approximation may be found if one accepts Van der Waal's equation $P = \frac{RT}{(v - b)} - \frac{a}{v^2}$

$$P_2 - P = \frac{\frac{2H}{R} \cdot \frac{M}{P_1}}{\frac{RT}{P} - \frac{2a}{RT} + b}$$

3° One reaches explicit calculations near the critical point. At temperature T close to T_c , a drop with radius R_0 causes a vapor pressure P_2 and an excess pressure P_1 in the liquid resulting in

$$\frac{P_2 - P}{P_c} = \sqrt{\frac{32}{15}} \left(1 - \frac{T}{T_c}\right) \frac{\sigma}{R_0}, \quad \frac{P_1 - P}{P_c} = 2 \sqrt{\frac{32}{15}} \left(1 - \frac{T}{T_c}\right)^{\frac{3}{2}} \frac{\sigma}{R_0}.$$

One observes that $P_1 - P_2$ is much less than $P_2 - P$ in this case. Moreover these values are extremely low because the surface tension is eliminated at the critical point, as $(T_c - T)^{3/2}$. These results are quite out of the reach of classical thermodynamics. The numerical coefficient $\sqrt{32/15}$ would undergo slight changes with the use of basic equations other than Van der Waals'.

It should be noted in connection with the size order, that the large ions $R_0 = 0.6 \times 10^{-5}$ cm in the case of water vapor lead far from the critical point, to $P_2 - P = 0.02 P$ while the saturation which may reach 8P in well dusted Wilson chambers, corresponds to a R_0 slightly superior to a molecular diameter.

*Trans. by Stancioff
fr. the French*